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To: Dr. D. Mills
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TRITIUM SEPARATION BY LASERS

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The status of the laser tritium separation project is summarized and a description of the work required to demonstrate the process with pilot plant scale components is discussed. It is estimated that this work can be done within three years. This report is based on a proposal submitted to CFFTP.

1.0 INTRODUCTION

Investigations into the separation of hydrogen isotopes are an ongoing area of experimental and theoretical studies in the Science Section at Research Division /1-10/. The early studies examined the production of heavy water by laser enrichment of a deuterium-carrying gas, and were later turned to the separation of tritium. Most of these studies, which can be divided for convenience into process chemistry and laser dissociation, were directly applicable to tritium separation with minor adjustments. (See for example, Reference 32.)

One adjustment in the laser dissociation step was to find a laser wavelength suitable for dissociating tritium-containing gas molecules while leaving hydrogen-containing molecules relatively untouched. Such a wavelength was found by tritium research workers based in Japan and the United States /11-15/, and was tested at Research Division in a new type of laser cell /16/. In this cell a capillary glass tube is employed as a waveguide to confine the laser energy and provide an extended volume of high energy fluence to dissociate the gas molecules. A computer model of laser dissociation in a waveguide cell has been developed and is being used for designing further experiments /17/.

The previous measurements of fundamental constants related to the process chemistry are applicable to both deuterium and tritium separation processes with the results for tritium expected to be more favourable than those for deuterium /19-22/. The main goal of recent chemical investigations has been to characterize completely the steps required to transfer the isotope of interest from water to trifluoromethane. This has involved determining the equilibrium constants and rate constants for the exchange processes.

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These constants are required for computer models of the process chemistry which will be combined with the model of the laser dissociation and used to optimize conditions for the tritium separation process.

The next step in the development of a laser-based tritium separation process is to construct pilot plant scale units, measure their performance, and study the difficulties of integrating the various units of the process. This report is based on a proposal submitted to the Canadian Fusion Fuels Technology Project to request funding for this next stage, and also represents a summary of the results obtained to date.

2.0 PROCESS DESCRIPTION

There are two main applications for tritium separation processes depending on the end product wanted--tritium enrichment (concentration) or the cleanup of tritium-contaminated waste streams. The basic physical principles and much of the hardware are the same in both cases but the process flowsheets have important differences.

The tritium separation process has three main functional areas--the exchanger, the laser dissociation cell, and the tritium separator. The exchanger unit consists of one or two parts, depending on the application. Both parts are required for the tritium enrichment process, whereas only the second unit is required for the tritium cleanup process. The first unit exchanges isotope-depleted water with isotope-rich water while maintaining catalyst concentrations constant. The second unit is common to both processes, and in this unit, a tritium-containing water stream is contacted by a stream of trifluoromethane (CF_3H) and the tritium transfers to the trifluoromethane.

The next area is the laser dissociation cell. A carbon dioxide laser is tuned to selectively break up only tritium-containing molecules (CF_3T) and the tritium-containing product of this dissociation process, tritium fluoride (TF), is then absorbed in the tritium separator on a sodium fluoride bed in a manner similar to water removal from air by a molecular sieve dryer. The undissociated trifluoromethane is recycled back to the tritium exchange tower to pick up more tritium. The selective dissociation takes place in a waveguide cell (Figure 1) which optimizes the use of laser photons in the laser process without undue stress to the mirrors and windows. We have applied for a patent on this cell design and have already been granted two patents on other parts of the process.

The isotopic selectivity of the tritium dissociation process is greater than 10 000 and likely exceeds 20 000. This means that a process designed to enrich tritium can, for example, convert a 10 ppm feed stream to an 8% product stream in a single step. If 99% tritium is required, a small finishing step using more conventional technology (eg cryogenic distillation or gas chromatography) or an additional laser stage would be required. The high single stage isotopic selectivity of the laser process means that a laser-based tritium enrichment process can have an extremely low tritium inventory.

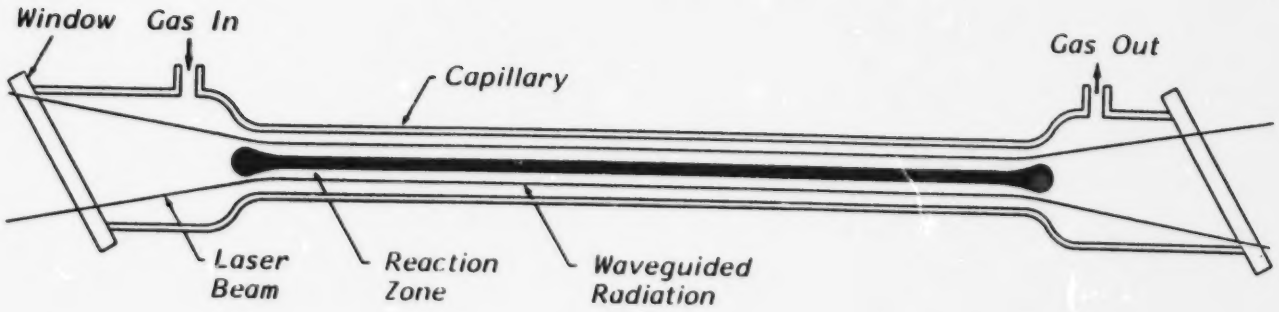

FIGURE 1

CAPILLARY WAVEGUIDE DISSOCIATION CELL
THE WAVEGUIDE CELL STRETCHES OUT THE HIGH FLUENCE REACTION ZONE, INCREASING YIELD.

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3.0 DIFFERENCES BETWEEN TRITIUM ENRICHMENT AND TRITIUM CLEANUP

3.1 Tritium Enrichment System

The goal of the enrichment process (Figure 2) is to maximize the tritium concentration in a small volume product stream and it is unimportant whether or not there is tritium in the waste stream. It is generally uneconomical to strip more than 90% of the tritium from the feed stream. More stripping can be done but the tritium concentration in the product is reduced. Similarly, higher single stage enrichments can be obtained if less than 90% stripping is specified.

For tritium enrichment, the tritium is transferred from the feed into a closed loop containing the exchange liquid. (The exchange liquid consists of water, catalyst and (optional) solvent.) The transfer is accomplished by bubbling the feed as water vapour through the exchange liquid in a counter-current flow column similar to but smaller than the exchange column described above. The feed is processed in seconds and is depleted in tritium but is not tritium-free. The exchange liquid which contains the correct catalyst concentration to promote rapid tritium exchange with trifluoromethane, is then pumped to the exchange tower where the tritium is transferred to the trifluoromethane process gas. The process then continues as described above (section 2.0).

3.2 Tritium Cleanup System

When a cleanup system is designed (Figure 3), the objectives are the reverse of an enrichment system. Instead of maximizing the product concentration with the waste concentration being unimportant, the waste concentration is minimized with the product concentration being unimportant. Several changes are made to the flowsheet to accomplish these goals. First, more laser pulses enter the trifluoromethane gas to remove the tritium, since tritium reductions of four orders of magnitude or more are required. It is likely that such reductions would require more than a single pass through the laser dissociation cell. Therefore the process is redesigned so that there is a second chance to remove the tritium. The feed-water exchange tower is replaced by a storage tank. The tank is filled with the feed water and the catalyst and (optional) solvent and this solution is pumped through the exchange tower where most of the tritium is removed by exchange with the trifluoromethane process gas. The exchange liquid is returned to the storage tank. If the tritium concentration is too high, the process can be repeated until the tritium cleanup specification is met. Because of the large isotopic selectivity of this process, it is expected that tritium levels will be lowered orders of magnitude below those achievable by conventional processes such as cryogenic distillation.

4.0 CURRENT STATUS OF PROCESS DEVELOPMENT

We have measured most of the physical and chemical constants required to model the process, and we have demonstrated several bench scale process components. Although the laser enrichment experiments have been demonstrated using tritium, all the process chemistry experiments have used deuterium as a substitute for tritium. We are confident that any performance measured with deuterium will be better when tritium is substituted. To demonstrate the effectiveness of laser tritium enrichment we must scale up the size of the

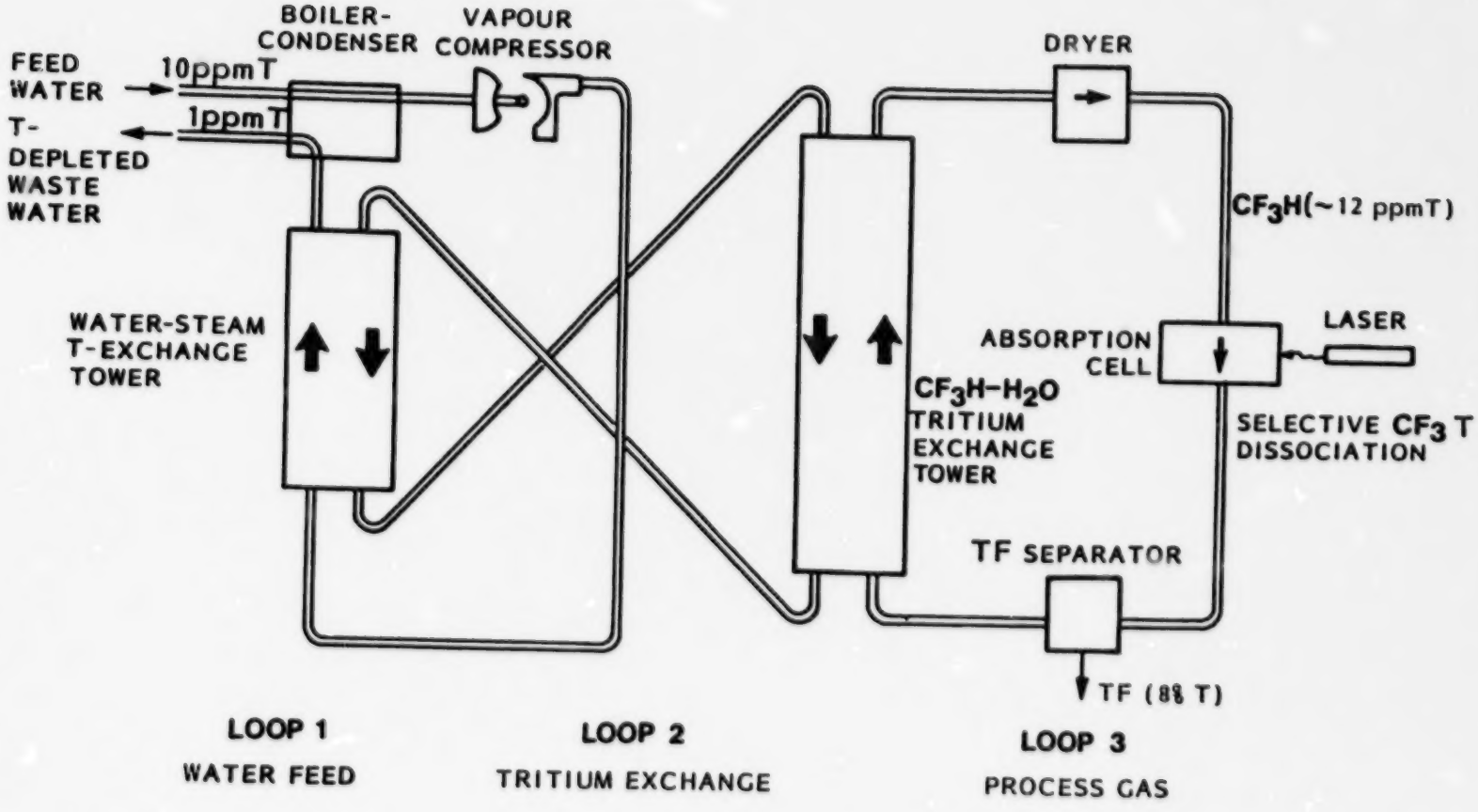

FIGURE 2

TRITIUM ENRICHMENT SYSTEM

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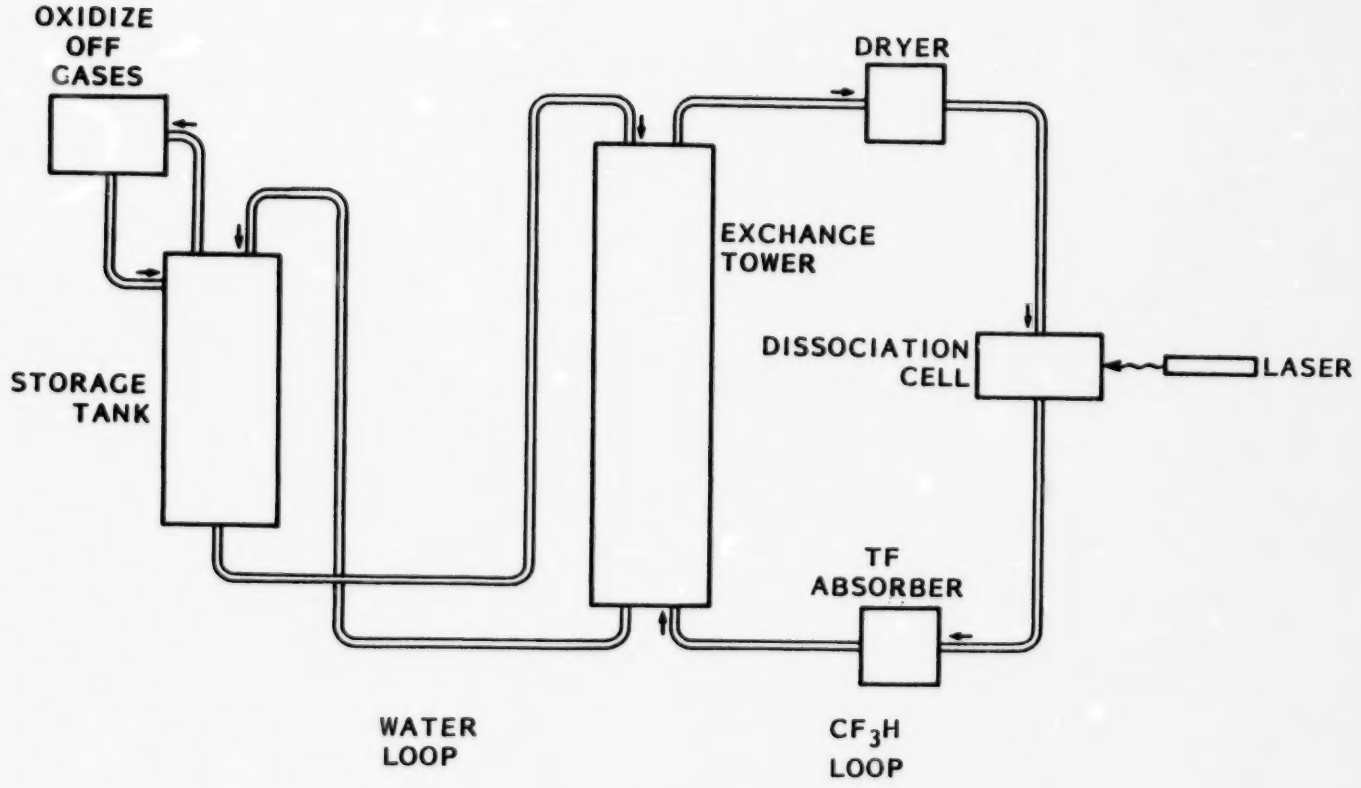

FIGURE 3
TRITIUM CLEANUP SYSTEM

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components and expand the use of tritium in our experiments. We must also study the problems involved with integrating the various process components.

4.1 Status of Laser Dissociation Experiments

1. We have confirmed that there are only two dissociation products of CF_3T, namely TF and C_2F_4. It is important to the TF separation step that all the T be in a single dissociation product. This was not the case for several other process gases that were considered.

2. The dissociation selectivity for CF_3T in CF_3H exceeds 11 000 and probably exceeds 20 000. This factor determines the product concentration of a laser enrichment stage and determines the amount of CF_3H make-up gas required.

3. We have developed the waveguide design for laser dissociation cells.

4. We have demonstrated the operation of a 1 mm diameter waveguide.

5. We have developed a computer model to describe the operation of waveguide laser dissociation cells.

6. We have measured the absorption spectrum of CF_3H and CF_3D in the 5 micron wavelength region to estimate the selectivity for separating T from both H and D in this region /18/. All other work was performed using lines from the 9 micron band of the carbon dioxide laser.

4.2 Status of Process Gas Exchange Experiments

We have measured a large number of fundamental chemical parameters using deuterium-containing compounds to model the performance of tritium-containing compounds and have combined these results with measurements made at AECL, Lawrence Livermore, and in Japan /14,15,23-30/.

1. We have measured exchange rates as a function of temperature, pressure, and exchange liquid composition.

2. We have measured the equilibrium constant for the D/H isotopic exchange reaction as a function of temperature, pressure, and exchange liquid composition.

3. We have measured the solubility of CF_3H as a function of temperature, pressure, and exchange liquid composition.

4. We have measured CF_3H decomposition rates as a function of temperature, pressure, and exchange liquid composition.

5. We have developed techniques for removing F^- ions from solution. These ions result from CF_3H decomposition and could increase equipment corrosion if not removed. A small slipstream (not shown) on the exchange liquid loop may be required.

6. We have demonstrated DF recovery as a function of temperature and pressure /31/.

7. We are developing a computer program to model and cost all aspects of this process.

5.0 DESCRIPTION OF THE NEXT STAGE OF THE PROJECT

The main effort in the next stage of the work will be to produce pilot scale components for the various parts of the isotope separation process. These individual components will be constructed and tested separately, and then integrated to the extent that physical constraints on the apparatus permit. All the process chemistry components will be integrated as the final step, but the laser will not be integrated with the rest of the components at this time because it is not large enough to handle the gas loads of pilot scale exchange towers.

5.1.1 Exchange Experiments

1. The major effort will be in the design, construction, and testing of the exchange tower. This tower is common to any version of the tritium exchange system and at most there would be minor variations for this tower depending on whether or not dimethyl sulphoxide is used as a rate-enhancing solvent. There may be some dimensional changes, and without dimethyl sulphoxide the operating temperature would be much higher. The experiments would involve development of flow control for both gas and liquid flows through the column, determination of the appropriate packing, and the optimal flow rates. The tests on the performance would be performed with water enriched in deuterium and the trifluoromethane would be stock gas from a cylinder. The performance would then be determined by measuring the efficiency of stripping of deuterium from water by trifluoromethane. It may also be necessary to operate the tower at elevated pressure to increase the efficiency of the transfer process. Once the tower is thoroughly tested, we can demonstrate its operation using trace quantities of tritium.

2. Two sets of measurements will complete the data sets required to properly model the behaviour of the chemical processes. The first is the extension of the rate constants for the transfer of hydrogen isotopes from water to trifluoromethane to slightly higher temperatures, with base present, but without dimethyl sulphoxide. We also require a few additional measurements of the rate constants for the transfer of hydrogen isotopes between water and dimethyl sulphoxide, in order to have a complete set available for the calculations.

   In addition, some measurements on the value of the equilibrium distribution of tritium between water and trifluoromethane will be made. At present, we have only deuterium-hydrogen equilibrium data which sets a lower limit on the tritium-hydrogen results. The measured rate and equilibrium constants can then be added to the modeling program to design the next set of experiments.

3. In low level cleanup in which dimethyl sulphoxide is used as a solvent to enhance exchange rates, there is the risk of a small amount of breakdown of this solvent with the attendant problems of having produced tritium-containing gases. Therefore the space above the storage tank will collect these gases (once the saturation pressure is reached) and it will be necessary to destroy these gases to prevent their release. The

most efficient method would appear to be the conversion of the gases to water by passing them over a hot metal oxide (eg cupric oxide). The tritium would then be converted back to water, and this water would simply be added to the tank for processing. The main experiments in this section would be to identify the most suitable metal oxide for the decomposition of the gases, and then to determine the operating conditions to ensure complete breakdown of the gases.

4. A component in determining the overall efficiency of the process is the efficiency of the sodium fluoride bed in trapping the TF product. The gas stream emerging from the laser dissociation cell contains a mixture of undissociated gas and the decomposition products. The HF/TF products are absorbed on the sodium fluoride beds and thus removed from the gas stream. Any TF that is still in the gas stream when this stream enters the exchange tower will dissolve in the water and rapidly exchange the tritium with water. The net effect is to reduce the overall efficiency of the process because the net quantity of tritium removed by a single pass through the laser cell is reduced. Previous experience indicates that the removal efficiency is high, but a quantitative measure of this efficiency is necessary for the calculations on the process as a whole.

5. In the case of tritium enrichment, another tower is required to process the feed water (section 2.0). Essentially this tower mixes the feed water with sodium hydroxide while simultaneously removing the tritium depleted water that comes from the trifluoromethane exchange tower. Some calculations must be done on this design to minimize costs. Previous experience in studying laser enrichment of deuterium has indicated that simply boiling the water to separate water, sodium hydroxide, and optional organic solvent was not economical. Our research program will have to determine whether this is still the case when we consider the higher value of the tritium product and the much lower throughput of the process.

5.1.2 Tasks - Process Development

1. Design and construct the exchange tower to operate under a variety of flow and pressure conditions.

2. Select a suitable packing for the tower and test the operation of the tower with enriched deuterium samples. These tests must be done with both high temperatures (water and sodium hydroxide only) and lower temperatures (water, sodium hydroxide, and dimethyl sulphoxide).

3. Design and construct a tower to transfer tritium from the feed to the exchange liquid.

4. Test this tower under atmospheric and subatmospheric operating pressures to minimize organic solvent decomposition.

5. Design and construct a unit to recover TF at the lowest possible TF vapour pressure. Measure the performance of this unit as a function of the (subambient) operating temperature.

6. Design, construct, and test a unit to oxidize to water any tritium-containing gaseous by-products of this process.

7. Develop a process control strategy and integrate the above components. Identify any process control problems.

8. Refine the computer programs that model and cost the process.

5.2.1 Laser Dissociation

The main questions to be answered by the laser dissociation work is how well does the process scale to larger waveguides? In this case larger means both greater diameter and length; diameters between 1 and 10 mm, and lengths between 0.4 and 5 m will be studied.

1. To investigate dissociation in large waveguides a new gas flow system is required to handle a greater range of gas volume and flow rates without oil contamination. The present flow system employs displacement of oil in contact with the gas to move it at constant pressure and rate through the dissociation cell. We plan to build an oil-free flow system that will use a regulator and needle valve to maintain constant pressure and flow rate. This system will eliminate the problems of oil contaminating the gas and of handling tritium contaminated oil. Another benefit will arise from the experience gained in using flow control components that are similar to the components that will be required in a pilot scale or full scale plant. The new flow system would be tested on a small waveguide cell (1 mm diameter, 40 cm long) and dissociation measurements compared with previous results to ensure that all components of the laser process are operating properly. During this phase, we also expect to test scintillation counting as a method for more sensitive detection of tritium than the present method which uses an ion chamber. Scintillation counting would be developed as part of the process chemistry instrumentation.

2. The first step in moving to larger waveguide cells is to build a 2 mm diameter cell. This is the largest diameter for which the present laser system can provide the full range of pulse energies necessary to characterize tritium separation as a function of energy. An extensive series of measurements would also provide data for optimizing the operating temperature and pressure of the gas in any cell. The next step is to measure dissociation in 2 mm diameter waveguides that are several meters in length. These tests will indicate how long a waveguide cell must be to use the laser energy most effectively.

3. Waveguide cells 2 mm diameter and larger must be tested for optimizing the coupling of laser energy into the cell and for their performance as waveguides. Some dissociation would be measured in a 3 mm diameter cell, but larger diameters would only be tested by examining the mode of propagation of laser energy through the cell. Another design consideration is the length of the window section required before the waveguide to maintain the laser energy fluence at the window below the threshold for damage. The minimum window section length scales with the area of the waveguide. Thus, cell design for a pilot scale plant must consider overall cell dimensions and options for integrating the laser dissociation with the process chemistry.

4. With the development of larger waveguide cells and tests on their performance, the computer model of the waveguide dissociation process can be refined. In turn the model will be used as an aid in designing experiments and to optimize designs for a pilot scale plant.

5.2.2 Tasks - Laser Dissociation

1. Design and build a new gas flow system for the laser dissociation cell.

2. Compare operation of the new and old gas flow systems by measuring the CF_3T dissociation in 1 mm diameter, 40 cm long waveguides.

3. Build a 2 mm diameter waveguide cell 40 cm in length.

4. Measure the CF_3T dissociation in the 2 mm diameter waveguide. Optimize the laser energy coupling into the waveguide, the operating temperature of the gas, and the operating pressure.

5. Design and build a longer 2 mm diameter waveguide up to 5 m long. Measure its performance for dissociation.

6. Design and build a 3 mm diameter waveguide cell. Measure its performance for dissociation.

7. Test laser energy coupling into larger diameter waveguides (up to 10 mm).

8. Refine the computer model of the waveguide dissociation process.

9. Investigate the design options for integrating large waveguide cells into a pilot scale plant.

6.0 SCHEDULE

We propose a three year program running from 1987 to 1989 to scale up and demonstrate process components and to integrate the various chemical process units. In order to minimize capital costs for this stage of our process development program, we plan to modify our existing laser system to maximize the output power.

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